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13. ABSTRACT (Maximum 200 words)

Proton-exchange membranes for direct methanol fuel cells were prepared from sulfonated poly[bis(3-methylphenoxy)phosphazene] and sulfonated poly[bis(phenoxy)phosphazene]. The methylphenoxy polymer was blended with Kynar® Flex and solution cast into thin films, whereas the bisphenoxy material was blended with polybenzimidazole (for acid-base complexation crosslinking) prior to membrane casting. Some of the films containing poly[bis(3-methylphenoxy)phosphazene] were UV-crosslinked for added control of swelling and methanol permeability. For most membranes, the proton conductivity was sufficiently high for direct methanol fuel cell (DMFC) applications but the methanol permeability was significantly lower than that in DuPont's Nafion. Membranes composed of sulfonated poly[bis(phenoxy)phosphazene] (SPOP) and polybenzimidazole (PBI) worked particularly well in a DMFC (at 60°C 1.0 M methanol, and ambient pressure air). Membrane performance in a DMFC was dependent on the blend composition (ion-exchange capacity of SPOP and wt% of added PBI). For an 82 μm thick membrane composed of 1.2 mmol/g IEC SPOP with 3 wt% PBI, the maximum power density was 89 mW/cm² (versus 96 mW/cm² with Nafion 117), while the methanol crossover was 2.6-times lower than that with Nafion 117.

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R. Wycisk, J.K. Lee and P.N. Pintauro, "Sulfonated Polyphosphazene-Polybenzimidazole Membranes for Direct Methanol Fuel Cells," *Journal of the Electrochemical Society*, **152**, A892-A898 (2005).

R. Wycisk and P.N. Pintauro, "Sulfonated Polyphosphazene Membranes for Direct Methanol PEM Fuel Cells," in Phosphazenes: A Worldwide Insight, M. Gleria and R. DeJaeger (Eds.), Nova Science Publishers, Hauppauge NY (2004).

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1. OBJECTIVE

The objective of this project was to fabricate and test sulfonated polyphosphazene membranes for use in a direct liquid methanol fuel cell. Workplan tasks included polymer functionalization (sulfonation), membrane preparation and characterization, membrane-electrode-assembly fabrication, and fuel cell tests. Two general classes of membranes were prepared and evaluated: (i) blends of a sulfonated polyphosphazene (with crosslinking groups) and an inert (uncharged), mechanically tough polymer and (ii) acid-base blends of a sulfonated polyphosphazene and polybenzimidazole.

2. BLENDS OF SULFONATED POLYPHOSPHAZENE AND AN INERT POLYMER

Our strategy for polyphosphazene membrane preparation was to blend a sulfonated and crosslinkable polyphosphazene with a mechanically tough and chemically resistant polymer and then crosslink the polyphosphazene component using either UV light or e-beam radiation. Out of several polyphosphazenes studied, sulfonated poly[bis(3-methylphenoxy)]phosphazene (henceforth abbreviated as SMPOP) was selected as the most suitable for crosslinking. The repeating monomer structure of this polymer is shown in Figure 1a.

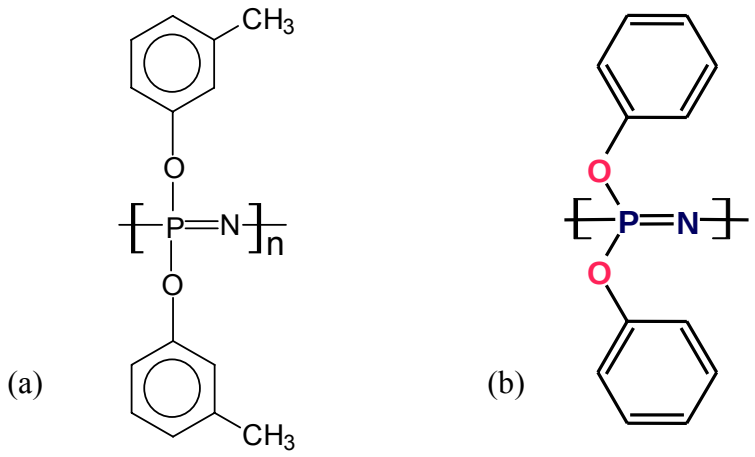

Figure 1 - The chemical structure of (a) poly[bis(3-methylphenoxy)phosphazene] and (b) poly[bis(phenoxy)phosphazene]

Preliminary results indicated that Kynar™ Flex (a copolymer of vinylidene fluoride and hexafluoro propylene) or polyacrylonitrile (PAN) were the best choice for the inert component of a blended membrane.

It has been shown previously that SMPOP could be crosslinked with benzophenone (BP) when irradiated with UV light of wavelength 365 nm. It was not obvious, however, whether it would be possible to: (1) create a useful blend by mixing SMPOP with a particular inert polymer, and (2) crosslink the SMPOP component of the blend.

It was found that, in general, Kynar Flex and PAN were immiscible on a molecular level with the SMPOP. The inert polymers had, however, an acceptable degree of compatibility and blends showed no signs of macroscopic phase separation for a relatively

wide composition range. The degree of compatibility increased with increasing ion-exchange capacity (IEC) of the SMPOP. Also, when the sulfonic acid groups of the SPOP were converted to the tetrabutylammonium (TBA) form, highly homogeneous, transparent blends were obtained. SPOP polymers in the Na^+ form produced better (more homogeneous) membranes than those in the acid form, although they were not as transparent as those made with TBA-substituted SMPOP.

From preliminary experiments of equilibrium water swelling and proton conductivity, it was found that the useful range of the effective ion-exchange capacity of the blended membranes should be between 0.95 and 1.2 mmol/g. These ion-exchange capacities could be obtained in two ways. First, by blending SMPOP of moderate IEC (1.4-2.2 mmol/g) with the inert polymer as a minor component, and second, by blending SMPOP of high IEC (2.5-4.0 mmol/g) with the inert polymer being the major component.

2.1 Experimental Results

The procedure for preparing blended SPOP membranes consisted of the following four steps:

(1) dissolving the membrane components (SMPOP in the Na^+ of Li^+ form, Kynar Flex or PAN and benzophenone) in N,N-dimethylacetamide (N,N-dimethylformamide solvent was used with PAN blends),
(2) casting a film on a flat surface and evaporating the solvent,
(3) crosslinking the SMPOP component of the membrane with UV light,
(4) converting the sulfonate ion-exchange groups to the acid form by soaking the film in H_2SO_4 followed by numerous washings with water to remove excess acid.

Initially, many batches of SMPOP were synthesized (using SO_3 as the sulfonating agent) with various IECs in the range 0.9-3.7 mmol/g. For the purpose of blending, three sulfonation degrees were selected for further studies, namely: 1.6, 2.1 and 3.5 mmol/g. For MEA preparation, some SMPOPs of lower sulfonation degrees (1.0-1.4 mmol/g) were also synthesized (these sulfonated polymers were used as catalyst binders during MEA fabrication, as will be discussed below).

Figure 2 shows the dependence of the IEC on the degree of sulfonation and also on the limits of water solubility of the SMPOP. At an ion-exchange capacity of 3.0 mmol/g, there is one sulfonic acid ion-exchange group per repeating monomer unit, whereas the addition of one SO_3H group to each methylphenoxy ring (two sulfonate sites per monomer unit) would result in an ion-exchange capacity of 4.8 mmol/g. SMPOP films with an IEC less than ≈2 mmol/g was insoluble in water at room temperature. On the other hand, polyphosphazenes with an IEC greater than ≈2. mmol/g were water soluble. Based on these preliminary sulfonation experiments, the following groups of membranes were synthesized:

Group 1	SMPOP(1.6 mmol/g)/PAN/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%
	SMPOP(1.6 mmol/g)/Flex/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%
Group 2	SMPOP(2.1 mmol/g)/PAN/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%

SMPOP(2.1 mmol/g)/Flex/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%

Group 3 SMPOP(3.7 mmol/g)/PAN/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%
SMPOP(3.7 mmol/g)/Flex/BP, effective IEC 0.9-1.2 mmol/g, BP 1-10%

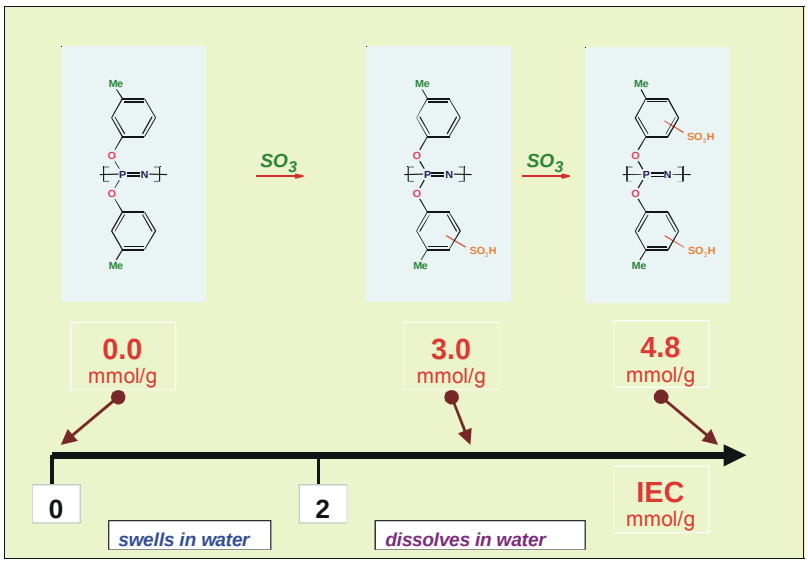

Figure 2 - Sulfonation of poly[bis(3-methylphenoxy)phosphazene]. Effect of Ion-Exchange Capacity (IEC) on water solubility.

Membranes belonging to Group 1 contained about 70% SMPOP. Their mechanical properties were not acceptable and macroscopic phase separation was frequently observed. Membranes belonging to Group 2 contained ≈50% SMPOP; their mechanical properties were acceptable and no phase separation occurred. Proton conductivities measured in water at 25°C ranged from 0.01 to 0.08 S/cm. Membranes belonging to Group 3 contained ≈30% SMPOP. No macroscopic phase separation was observed in dry films, however, the membranes lost SMPOP immediately after immersion in water. This was an indication of insufficient UV-crosslinking of the high-IEC SMPOP component of the blended film.

Most of our research was focused on membranes belonging to Group 2. Figure 3 shows SEM micrographs of the cross-sections of three samples of SMPOP/Flex membranes. The H^+ counterions in SPOP were substituted prior to blending with tetrabutylammonium (TBA), Na^+ or Cs^+ cations. It can be seen that the best compatibility between SPOP and Flex was achieved when SMPOP was in TBA form. It was, however, impossible to crosslink these blends (due presumably to steric interference by the bulky TBA counterions). Consequently, all follow-on studies were performed with SPOP in Na-form.

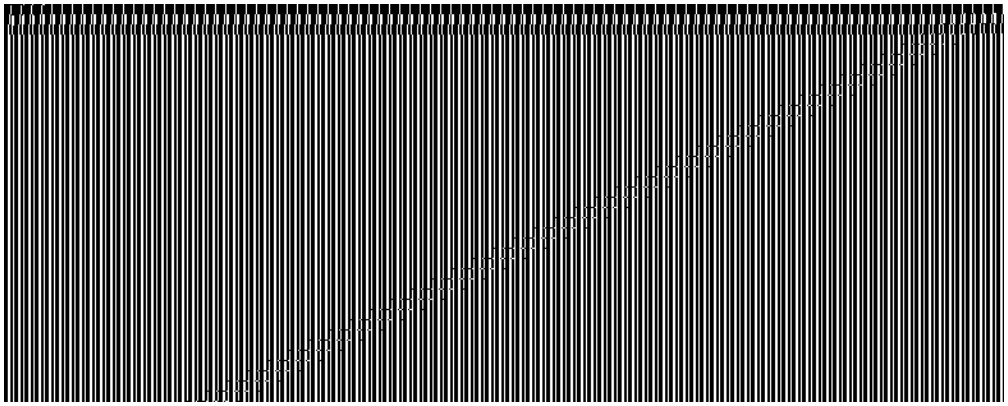

Figure 3 - SEM Micrographs of SPOP/Flex Blends, of different counterion form.

The most important properties of the blended membranes were their conductivity, water swelling, and methanol (MeOH) permeability. Figure 4 shows the dependence of proton conductivity on membrane swelling in water at 25°C for UV-crosslinked and electron-beam-crosslinked SMPOP/Flex blends. It can be seen that there is a linear correlation between the conductivity and swelling, which is independent of the method used to crosslink the SMPOP. It can also be concluded from this data that membranes with a wide range of conductivity and swelling can be synthesized.

In order to assess the methanol permeability of the blended SMPOP membranes, a membrane sample was placed in a fuel cell apparatus and an aqueous methanol solution was pumped past one side of the membrane. At the opposite membrane surface, a commercial Pt/C fuel cell cathode was pressed against the membrane and humidified air was circulated past the electrode. In such an arrangement, any methanol that permeated through the membrane would be chemically oxidized to CO_2 and water at the platinum catalyst. An electronic sensor (Vaisala GMM12B) placed in the downstream air line monitored the concentration of the CO_2 generated from methanol oxidation. The trans-membrane methanol flux was calculated from the air flow rate, the increase in CO_2 concentration over background air, and the membrane area exposed to the methanol solution. Representative steady-sate methanol flux data at 60^{o}C and 70^{o}C for two blended and UV-crosslinked polyphosphazene membranes (polyphosphazene blended with Kynar Flex) and for Nafion 117 are plotted against the methanol solution concentration in Figure 5. Taking into account the differences in wet film thickness (130-140 μm for the polyphosphazene membranes vs. 220 μm for Nafion 117), thickness-corrected methanol fluxes for the SMPOP membranes were 6-11 times lower than those obtained for Nafion 117.

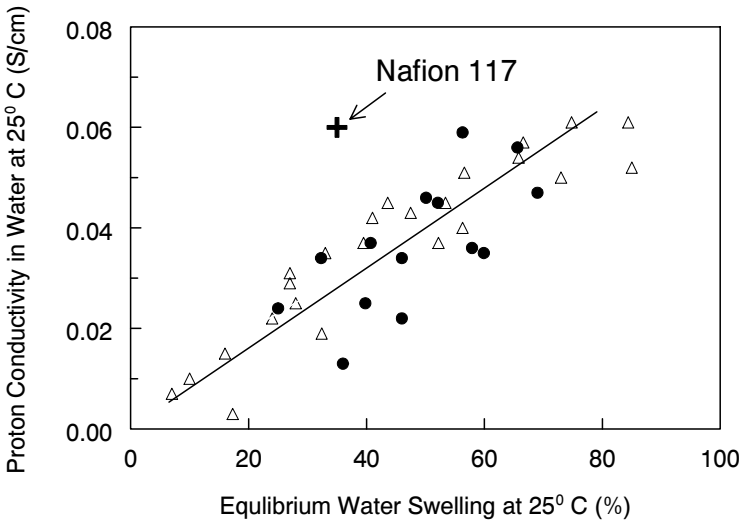

Figure 4 - Correlation of membrane proton conductivity vs. equilibrium membrane water swelling for SMPOP/Flex membranes. Conductivity measured by AC impedance for membranes immersed in water. Open triangles are UV-crosslinked membranes; solid circles are electron-beam-crosslinked films.

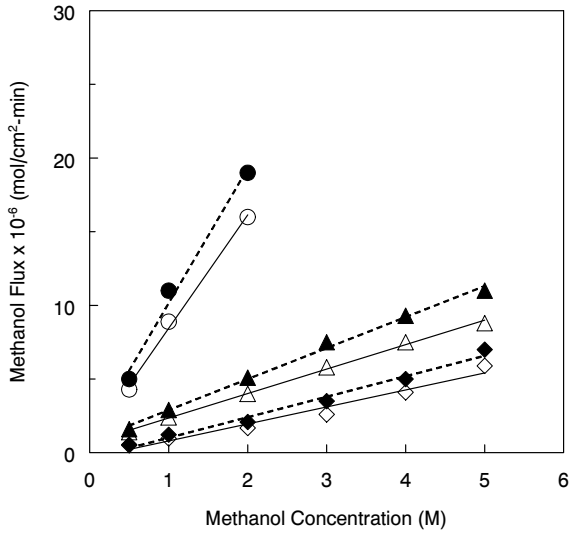

Figure 5 - Trans-membrane methanol flux for simple diffusion across Nafion 117 and blended SMPOP membranes.

▲ and Δ: SMPOP/Kynar Flex blend (52% 1.9 mmol/g IEC SMPOP + 48% Flex, crosslinked with 60 megarads of electron beam radiation; 130 μm wet thickness; κ=0.015 S/cm at 25°C);

, and : SMPOP/Kynar Flex blend (50% 2.0 mmol/g IEC SMPOP + 40% Flex + 10% difluorobenzophenone, crosslinked with UV radiation; 220 μm wet thickness; κ=0.037 S/cm at 25°C);

and : Nafion 117 (220 μm wet thickness). Solid symbols are data at 70°C, open symbols at 60°C.

2.2. Membrane-Electrode-Assembly Fabrication and Testing

Membrane-electrode assemblies (MEAs), for use in direct liquid methanol fuel cells were fabricated and evaluated using blended SPOP membranes. The objectives of this task were to identify polyphosphazene materials for use as membranes and as catalyst binders and to develop procedures for the fabrication of membrane-electrode-assemblies that could be used in direct methanol fuel cells. The research involved: (1) preparing catalyst inks with sulfonated poly[bis(3-methylphenoxy)phosphazene] as the polymeric binder and fabricating MEAs using these inks with a Nafion 117 cation-exchange membrane and (2) preparing MEAs with Nafion as the catalyst binder and a cation-exchange membrane composed of sulfonated poly[bis(3-methylphenoxy)phosphazene] that was blended with polyacrylonitrile and then UV-crosslinked.

2.2.1 MEA Fabrication with Nafion 117 Membranes and SMPOP Binder

Electrodes were prepared by one of two methods. In the first method, catalyst ink was painted onto a 5.0 cm^2 Teflon treated carbon cloth (ELAT, E-TEK) and the cloth was heated to 90^oC to evaporate solvent. For the air cathode, two distinct catalyst/binder layers were employed. The first layer used Teflon as the binder to minimize water flooding (2 mg/cm^2 Pt-black with 8% Teflon) and the second layer was 2 mg/cm^2 Pt-black with 10% SMPOP. The anode was 4 mg/cm^2 Pt-Ru with 10% SMPOP binder. The anode and cathode were hot-pressed onto a Nafion 117 membrane at 120^oC and 125 psi for 5 minutes. The second method used the so-called "decal" procedure for MEA fabrication. For the cathode, two catalyst inks were painted onto a 5 cm^2 Teflon blank (first a Pt/Teflon ink and then a Pt/SMPOP ink with a total catalyst loading of 4 mg/cm^2). For the anode, 4 mg/cm^2 Pt-Ru catalyst with 10% SPOP binder was employed. After evaporating the solvent, the decals were hot-pressed onto a Nafion 117 membrane at 120^oC and 125 psi for 5 minutes. The Teflon film blanks were then peeled off of the membrane, leaving behind adhered catalyst layers. Carbon cloth backing sheets were placed adjacent to the anode and cathode when the MEA was placed into the fuel cell test fixture.

SMPOP-based catalyst inks were prepared by dissolving sulfonated poly[bis(3-methylphenoxy)polyphosphazene] in either isopropyl alcohol or N,N-dimethylacetamide (DMAC). Water and catalyst (10 parts water to 1 part catalyst) were added to the polymer solution followed by extensive sonication. The final ink contained 10 wt% SMPOP (on a dry catalyst weight basis). Teflon/catalyst inks were prepared by mixing a commercial Teflon solution with a known weight of catalyst, followed by sonication.

The effect of SMPOP ion-exchange capacity (IEC) for the anode/cathode binder on fuel cell performance is shown in Figure 6 (1.0 M methanol fuel cell test at 60^oC). The best V-i curve was obtained with 1.2 mmol/g IEC SPOP binder. The 1.3 IEC SMPOP binder performed poorly, presumably due to excessive polymer swelling in 1.0 M methanol. Fuel cell performance with the 1.0 IEC SMPOP binder was also poor, for reasons not well understood at this time.

A comparison of the two MEA fabrication methods (standard hot press vs. decal) is shown in Figure 7. The decal method appears to work better, as noted by the higher cell voltage at a given current density.

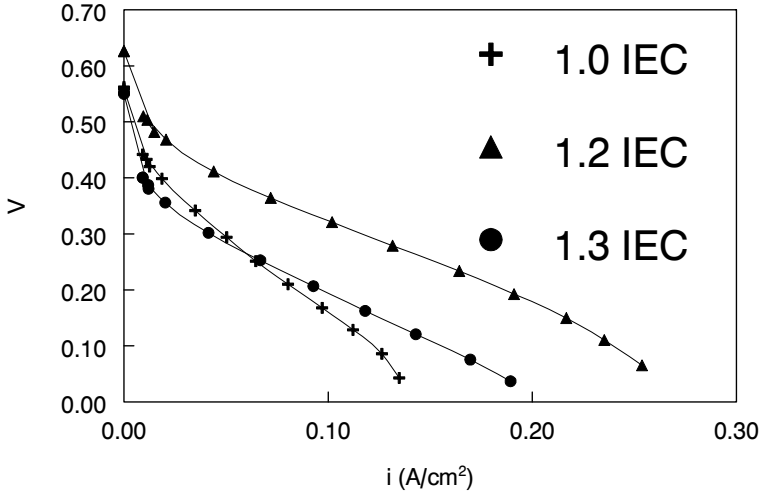

Figure 6 - The effect of SMPOP binder IEC on DMFC performance. Membrane: Nafion 117, Cell Temp. = 60°C; 1 M methanol; Air at 70°C, 600 SCCM and 30 psi; Anode = 4 mg/cm^2 Pt-Ru w/10% SMPOP binder; Cathode = 2 mg/cm^2 Pt-black w/8% PTFE binder + 2 mg/cm^2 Pt-black w/10% SMPOP Binder; electrode geometric area = 5 cm^2.

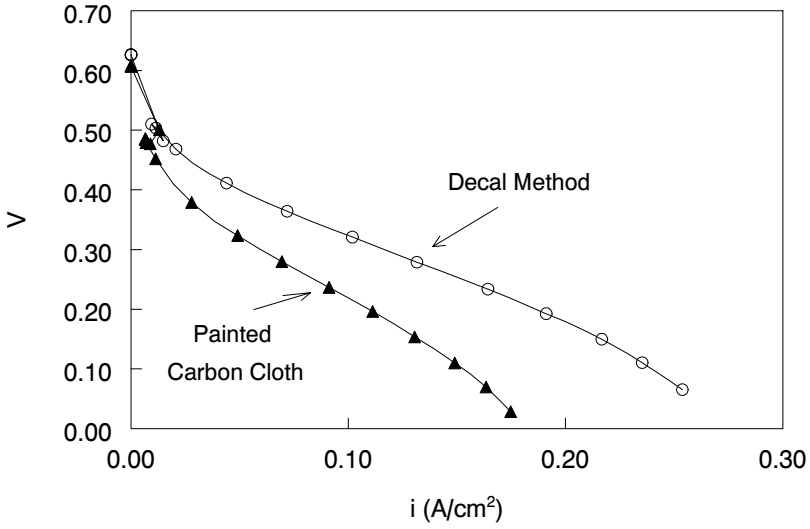

Figure 7 - Comparison of MEA Fabrication Methods. Membrane: Nafion 117, Cell Temp. = 60°C; 1 M methanol; Air at 70°C, 600 SCCM and 30 psi; Anode = 4 mg/cm^2 Pt-Ru w/10% SMPOP binder; Cathode = 2 mg/cm^2 Pt-black w/8% PTFE binder + 2 mg/cm^2 Pt-black w/10% SMPOP Binder; electrode geometric area = 5 cm^2.

3. POLYPHOSPHAZENE-PBI BLENDS

In this part of the research project, DMFC membranes composed of blends of sulfonated polyphosphazene and polybenzimidazole (PBI) were fabricated, characterized, and evaluated. In such acid-base blended membranes, H^+ transfer (partial or complete) between the proton-containing sulfonic acid sites of the polyphosphazene and polymeric basic moieties of the second component of the blend leads to the formation of ionic crosslinks which increase the osmotic stability (lower solvent swelling) of the resultant membrane. An additional advantage of the blends is the reduced membrane brittleness upon drying as compared to uncrosslinked or covalently crosslinked sulfonic acid phosphazene polymers.

3.1 Membrane Preparation

Proton-conducting fuel cell membranes were prepared from blends of sulfonated poly[bis(phenoxy)phosphazene] (hereafter denoted in this report as SPOP) and polybenzimidazole (PBI), where the latter, being the polymer base, was used as a crosslinking component. The repeating monomer unit for poly[bis(phenoxy)phosphazene] is shown in Figure 1b. A new method of sulfonating the phosphazene polymer, using concentration sulfuric acid, was developed and found to be superior to the use of sulfur trioxide, in terms of the uniformity of polymer sulfonation and the minimization of polymer degradation. The ion-exchange capacity (IEC) of membranes prepared from SPOP was controlled by the polymer exposure time to H_2SO_4; an increase in IEC from 0.95 to 1.35 mmol/g was achieved by increasing the sulfonation time from 95 to 120 minutes. Materials with an IEC less than 0.95 mmol/g had negligible conductivity (<0.001 S/cm) while films of IEC greater then 1.4 mmol/g were partially soluble in water. Blended membranes were prepared from SPOP with an IEC in the range 1.2-1.4 mmol/g, with PBI contents ranging from 2.5 to 12 wt%.

3.2 Membrane Properties

The dependence of room temperature proton conductivity on the PBI content of blended membranes (with 1.4 IEC SPOP) is shown in Figure 8. The undiluted SPOP polymer had a conductivity of 0.082 S/cm. The conductivity of the blended films decreased with increasing PBI due to: (i) PBI-SPOP crosslinks which reduce water swelling (i.e., the number of water molecules per sulfonic acid site), as shown in Figure 9 and (ii) the neutralization of some sulfonic acid groups in SPOP due to complexation with PBI (see Figure 10)

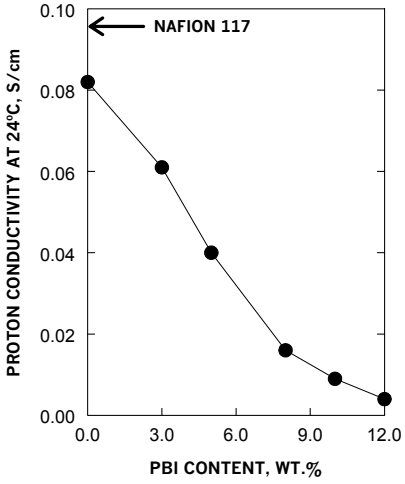

Figure 8 – The effect of PBI content on the measured proton conductivity (at 24°C) of water-equilibrated SPOP-PBI blended membranes. All membranes prepared with 1.4 IEC SPOP.

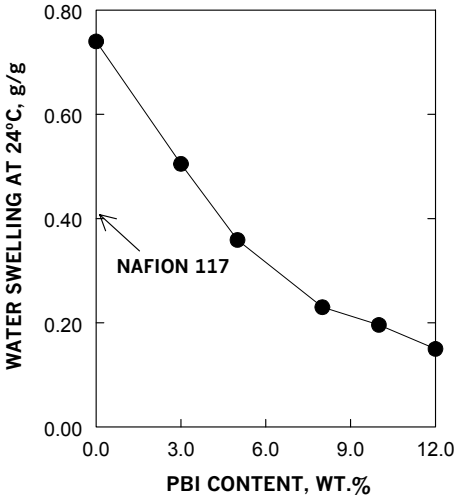

Figure 9– Effect of PBI content on equilibrium water swelling of SPOP-PBI blended films (1.4 IEC SPOP).

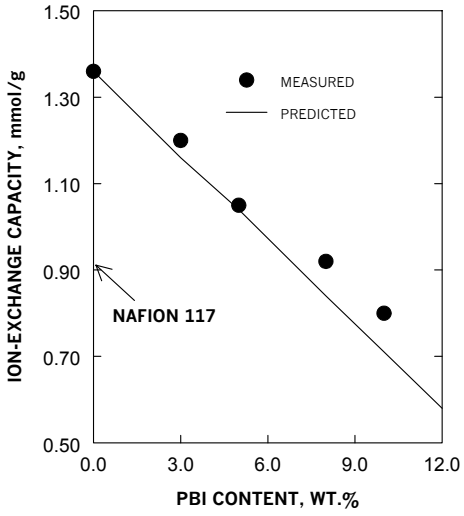

Figure 10 –Effect of PBI content on the effective IEC of SPOP-PBI blends (1.4 IEC SPOP).

The dependence of methanol permeability (measured with a 1.0 M methanol solution at 60°C in a custom-built diffusion cell) on the PBI content of SPOP-PBI membranes is shown in Figure 11. The permeability decreased from 2.0 x 10^{-6} cm^2/s (for a 1.4 IEC SPOP film with no PBI) to 1.0 x 10^{-7} cm^2/s (1.4 IEC SPOP with 12 wt% PBI). All measured permeabilities were significantly lower (1.75-35 times lower) than that in Nafion117.

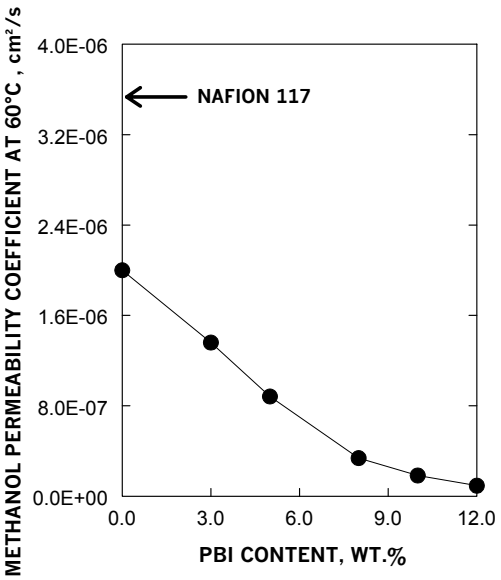

Figure 11 – The dependence of methanol permeability in SPOP-PBI blended films on PBI content (1.4 IEC SPOP)

3.3 Fuel Cell Tests

The electrochemical performance of membrane-electrode assemblies (MEAs) with blended SPOP-PBI films was evaluated using a standard (Scribner) fuel cell test station. Considerable time and effort was expended in developing a MEA fabrication technique that produced good fuel cell performance with the SPOP-PBI membranes. MEAs were prepared by hot-pressing catalytic electrodes (5 cm^2 area electrodes; Pt/Ru anode, Pt cathode; Nafion as the catalyst binder) to the opposing surfaces of a SPOP-PBI membrane (the hot-pressing conditions were: 80^oC and 63 psi pressure for 3 minutes). SPOP-PBI membranes were typically 80-120 μm in thickness (considerably thinner than Nafion 117). MEAs were evaluated first in a direct methanol fuel cell operating at 60^oC, with 1.0 M methanol and ambient pressure air. Typical electrochemical performance curves are shown in Figure 12. These results were collected after ca. 3 hours of fuel cell operation. Initially, all of the MEAs generated more power, but after a period of time (ca. 1 hour) the performance decreased slightly, due presumably to methanol crossover and oxidation at the air cathode, which poisoned, to some extent, the cathode catalyst. The experimental protocol used here is more realistic of actual fuel cell operation. The use of an initial V-i curve for evaluating an MEA in a DMFC is predicated on the assumptions that: (i) there is essentially complete methanol oxidation at the anode so that there will be no methanol crossover during long-term power generation at different loads and (ii) when idle (at open circuit), methanol is flushed from the anode feed channel and makes no contact with the MEA. Both of these assumptions are unrealistic from a practical viewpoint.

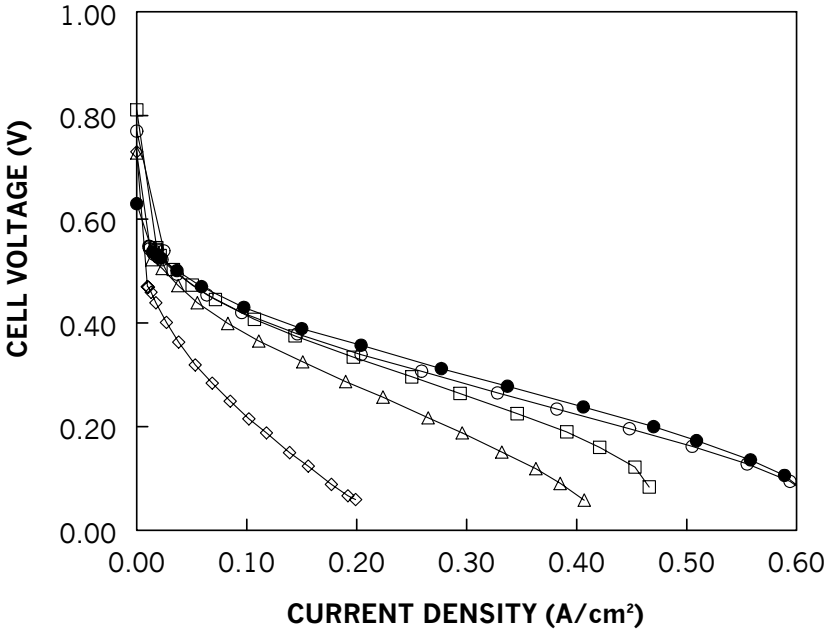

Figure 12 – Electrochemical performance of SPOP-PBI blended membranes in a direct methanol fuel cell (60°C, 1.0 M methanol, air at ambient pressure).

- ● Nafion 117; 220 μm thickness; methanol crossover=1.0
- ○ SPOP12-PBI02.5; 82 μm thickness; methanol crossover=0.41
- □ SPOP14-PBI05; 115 μm thickness; methanol crossover=0.33
- Δ SPOP12-PBI05; 120 μm thickness; methanol crossover=0.13
- ◊ SPOP14-PBI12; 95 μm thickness; methanol crossover=0.06

The performance data for an MEA with a blended film of 1.2 IEC SPOP (denoted as SPOP12) and 2.5 wt% PBI (PBI02.5) is particularly noteworthy. The voltage-current density curve with this blended membrane was essentially identical to that of Nafion 117, but the measured methanol crossover in the blend was 2.4 times lower than that in Nafion (methanol crossover was measured using a CO_2 sensor in the cathode exit air). With higher PBI content in a blended membrane, the methanol crossover decreased significantly (as low as 16.7-times lower than Nafion 117 with 12 wt% PBI), but the sheet resistance of the film (proportional to the membrane conductivity and thickness) was unacceptably high. The performance of a membrane containing 1.4 IEC SPOP with 5 wt% PBI was somewhat lower than that with Nafion 117, but the crossover was 3-times less than Nafion. It might be possible to improve the performance of this MEA by optimizing on the membrane composition/thickness and MEA fabrication procedure. Overall, the electrochemical performance curves in Figure 12 and the methanol crossover data measured during fuel cell operation show that SPOP-PBI blended films work as well as any DMFC membrane currently reported in the open literature.

The effect of methanol feed concentration on methanol crossover and overall fuel cell performance with SPO-PBI MEAs was assessed in a series of experiments. The effect of methanol feed concentration (1.0, 5.0, and 10.0 M) on DMFC voltage-current density plots is shown in Figure 13 for a SPOP13-PBI3 membrane (82 μm in thickness). For comparison purposes, a V-i plot for Nafion 117 (≈220 μm in thickness) with a 10.0 M methanol feed is also shown in this figure. For the polyphosphazene films, there is a modest loss in fuel cell power output when the methanol feed concentration is increased from 1.0 to 5.0 M, with a more substantial drop in power for the 10.0 M feed experiment. The decline in DMFC performance was attributed to an increase in the methanol crossover flux with increasing feed concentration (as would be expected). The SPOP-PBI membranes performed much better than Nafion 117, with a lower methanol crossover (2.5 times lower than Nafion 117 at all three methanol feed concentrations, even though the Nafion membrane was about 3 times thicker than the SPOP-PBI films) and significantly better V-i behavior.

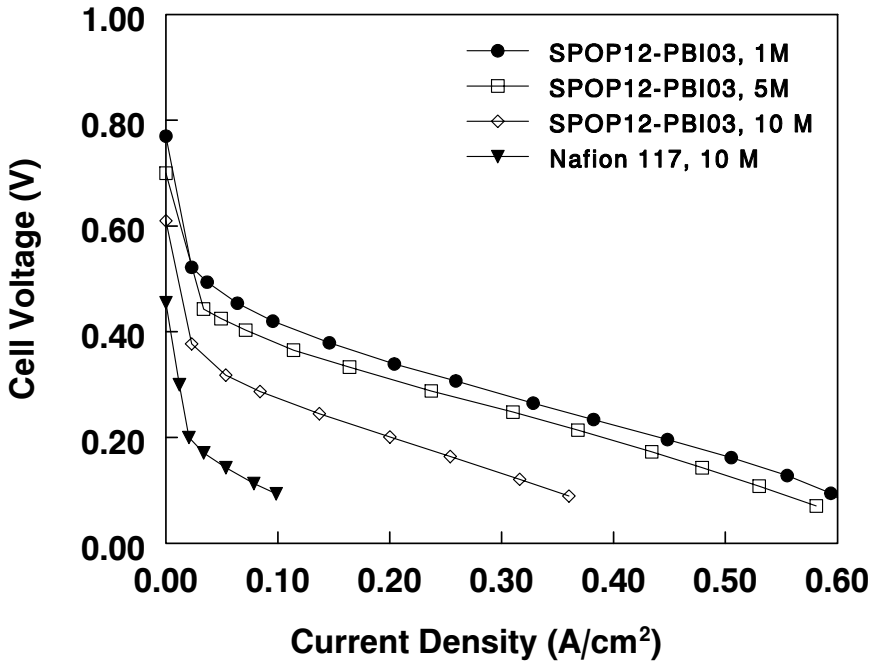

Figure 13 – Electrochemical performance of a SPOP12-PBI03 MEA in a direct methanol fuel cell at different methanol feed concentrations (60°C and air at ambient pressure and 500 sccm). SPOP-PBI membrane thickness was 82 μm.

- ● 1.0 M methanol (crossover relative to Nafion 117 at 1.0 M was 0.39).
- □ 5.0 M methanol (crossover relative to Nafion 117 at 5.0 M was 0.38).
- ◊ 10.0 M methanol (crossover relative to Nafion 117 at 10.0 M was 0.39).
- ▼ Nafion 117 at 10.0 M methanol (thickness ≈220 μm.

Methanol crossover flux vs. methanol feed concentration data were collected during DMFC tests with three different SPOP-PBI membranes (containing either 1.2 or 1.4 mmol/g IEC SPOP with 3%, 4% or 8% PBI). The thickness of each membrane differed. The resulting methanol crossover flux data (at 60°C and open circuit) are compared to results with a Nafion 117 MEA in Figure 14. All of the SPOP-PBI films were better barriers to methanol than Nafion 117, for methanol concentrations of 1.0-10.0 M, even though the polyphosphazene films were much thinner than Nafion. The relatively high methanol flux for the thick (141 μm) SPOP14-PBI04 film was due to this film's high IEC (1.4 mmol/g) which caused the membrane to swell more in methanol. When the PBI content of the membrane was increased from 4% to 8%, there was more acid/base crosslinking and the crossover flux was reduced by about one-half. Low methanol permeabilities were also obtained by lowering the SPOP ion-exchange capacity (from 14. to 1.2 mmol/g) and adding less PBI (3 %). The results in Figures 13 and 14 demonstrate that SPOP-PBI are an attractive membrane material for methanol fuel cells that must operate at high methanol feed concentrations.

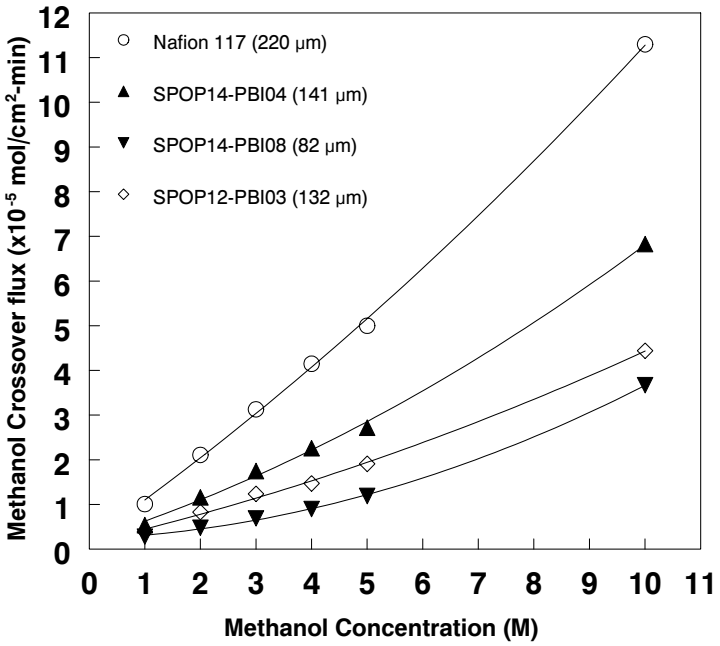

Figure 14 – Effects of methanol feed concentration and membrane composition on the methanol crossover flux, as measured at open circuit in a direct methanol fuel cell (T=60°C).

In a final series of experiments, the maximum power of a DMFC was determined as a function of methanol feed concentration for MEAs containing a SPOP-PBI membrane (1.2 IEC SPOP with 3.0 wt% PBI) and Nafion 117. DMFC tests were performed at 60°C with ambient pressure air and methanol concentrations of 0.25-5.0 M. The results of these

experiments are shown in Figure 15. As can be seen, the maximum power density with the SPOP-PBI membrane is much less sensitive to changes in methanol concentration, as compared to Nafion. This result was not unexpected, since PBI-crosslinking controls (restrains) the swelling of SPOP at all methanol concentrations. The precipitous drop in power at 4.0 and 5.0 M methanol with Nafion was due to excessive methanol crossover. The slightly higher DMFC performance with the SPOP-PBI film at 0.25 M and 0.5 M may be due to reduced mass transfer resistance of methanol (catalyst was hot-pressed onto the SPOP-PBI at a lower pressure and temperature, as compared to Nafion and there may be less catalyst penetration into the membrane for the polyphosphazene-based film). These results suggest that SPOP-PBI membranes can be used in a DMFC at moderately high methanol feed concentrations, without a significant loss in power output.

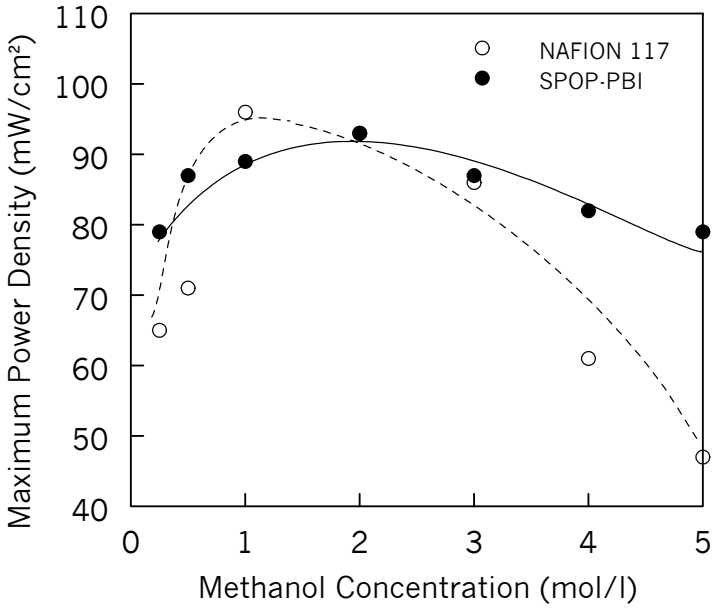

Figure 15 – Effect of methanol feed concentration on maximum power for a DMFC operating at 60°C with ambient pressure air at 500 sccm.

3.4 Long-term Fuel Cell Tests

Two types of lifetime tests were performed. First, swelling and conductivity of a SPOP14-PBI05 membrane in 1.0 M methanol at 60°C were measured periodically over 408 hours (17 days). It was found that the swelling increased slowly with time (from an initial value of 59%) and eventually stabilized at 125% near the end of the experiment. During this time, the proton conductivity remained unchanged (at 0.04 S/cm). The final dry weight of the membrane was the same as the initial weight, indicating no degradation or dissolution of the polymer. The constant conductivity showed that there was no dissociation of the sulfonate-imidazole crosslinks. The increase in swelling is indicative of the relaxation of the polyphosphazene structure upon an osmotic stress at elevated temperature.

In the second long-term experiment, an MEA was tested in a DMFC for 100 hours, at 60°C with 1.0 M methanol and ambient air. To extend the longevity of the electrodes, the fuel cell was operated in a load cycling mode, i.e., repeated cycling of 59 minutes with the current on (at 0.10 A/cm^2) and 1 minute at open circuit. During the cycling, the voltage was continuously recorded. The measured cell voltage decreased slowly for a PBI-doped polyphosphazene MEA, at a rate of approximately 0.8 mV/hour (from an initial value of 0.39 V to 0.31 V after 100 hours). Methanol crossover remained unchanged for the entire 100 hours. The initial cell voltage could be fully recovered by lowering the temperature to 25^{o}C and washing the membrane with deionized water for 2 hours (either by removing the MEA from the fuel cell test fixture or by an in-situ procedure where the methanol feed solution is replaced by room-temperature water). After this regeneration step, however, the cell voltage once again began to decrease. At the present time, the cause of the observed voltage loss is not known precisely, but may be due to cathode catalyst poisoning by CO (formed when methanol permeates through the membrane and is chemical oxidized at the cathode) and/or interfacial resistance between the membrane and the Nafion binder in the electrodes, which increases over time due to a growing difference in swelling between Nafion and the SPOP-PBI film. It may be possible to correct this problem by adjusting the membrane IEC and PBI content (i.e., adding more PBI to the blend should stiffen the membrane and minimize/eliminate the slow, upward drift in swelling by methanol). A typical voltage vs. time plot (with and without load cycling) for a long-term MEA test is shown in Figure 16.

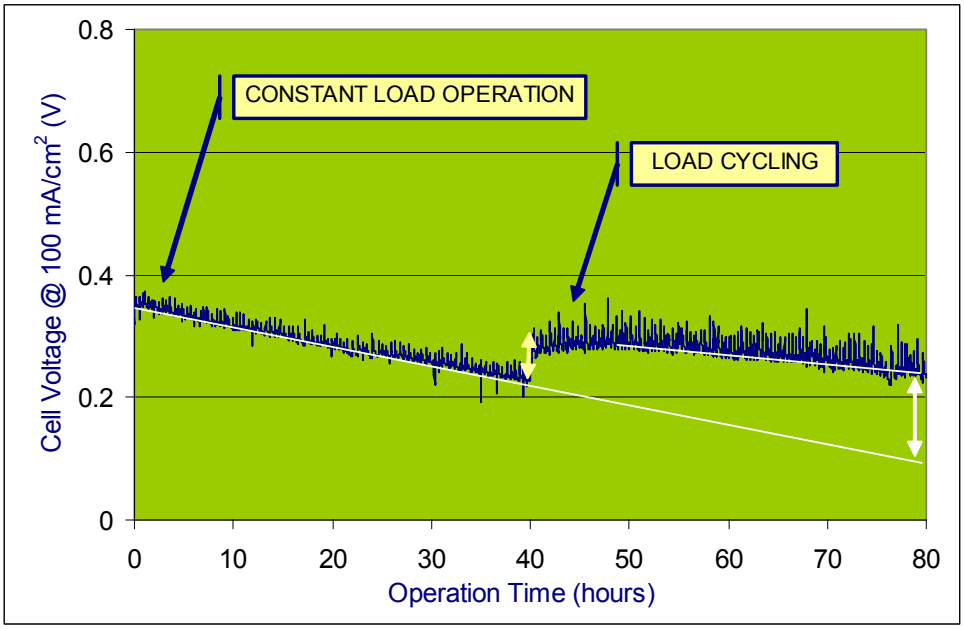

Figure 16 – Voltage vs. time plot for long-term MEA testing with an SPOP-PBI membrane. 1.0 M methanol 60^{o}C, 100 mA/cm^2 load.

3.5 Conclusions

Proton-conducting fuel cell membranes were prepared from blends of sulfonated poly[bis(phenoxy)phosphazene] (SPOP) and polybenzimidazole (PBI), where the latter, being a polymer base, was used as a crosslinking component. Depending on the SPOP ion-exchange capacity and the amount of added PBI, membranes had a room temperature proton conductivity in the range 0.01-0.08 S/cm, an equilibrium water swelling from 18-75% and a room-temperature methanol permeability (1.0 M methanol) that ranged from $1.2 \cdot 10^{-6}$-$1.2 \cdot 10^{-7}$ cm²/s. Membranes (82-120 μm in thickness) were tested in a direct methanol fuel cell, operating at 60ºC with a 1.0 M aqueous methanol feed solution and ambient pressure air.

Depending on the ion-exchange capacity of the SPOP (either 1.2 or 1.4 mmol/g) and the PBI content of the membrane (5% to 12%), the maximum DMFC power density with ranged from 23 to 89 mW/cm² (as compared to 96 mW/cm² with Nafion 117), while the methanol crossover was between 4.2×10^{-6} mol/cm^2-min and 5.9×10^{-6} mol/cm^2-min (versus 1.17×10^{-5} mol/cm^2-min with Nafion 117).

The long-term stability of the SPOP-PBI membranes was evaluated by means of methanol soak tests and continuous fuel cell operation. A slow, upward drift in membrane swelling, with no change in proton conductivity, was observed when blended films were soaked in 1.0 M methanol at 60^{o}C for 17 days. During a 100 hour DMFC test at 0.10 A/cm^2, the cell voltage decreased by approximately 0.8 mV/hr. The voltage loss was reversible; by exposing the MEA to room temperature water, there was complete recovery of MEA performance. The voltage loss has been associated with a growing contact resistance between the SPOP-PBI membrane and the Nafion binder in the electrodes due to the difference in swelling of the two polymers and/or cathode catalyst poisoning by CO (a product of methanol oxidation).

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